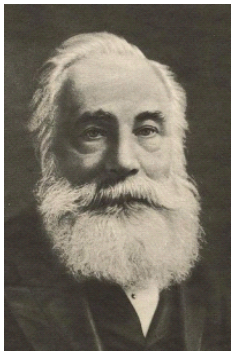
Fig. 30-1



William Henry Perkin (1838 - 1907)
Discovered first synthetic dye, mauve.
http://en.wikipedia.org/wiki/Sir_William_Henry_Perkin

Experiment 30

SYNTHESIS AND USE OF A DYE

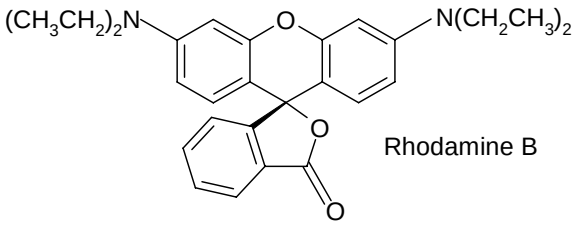
Text Topics and New Techniques

Friedel-Crafts reaction, dying of fabrics.

Discussion

Color is a very important attribute in chemicals and we need to consider how rare or common it is. Ask yourself what the most common colors of the solids and liquids are in your stockroom. Your answers should have been that the almost all the solids are white and the liquids colorless. Since color livens up our lives, we often add color to our environment by means such as painting, dying or adding plants. We even find food to be more desirable if it has aesthetically appropriate color. As a result, chemicals are added to food to preserve, introduce or enhance color. Would you want all of your M&M's to be one color or your meat to be a drab brown? When food or clothes or any part of our environment that we interact with is artificially colored, we must be careful that the chemicals used are not potentially harmful to animals and plants. Most inorganic ions that are colored such as Ni^{2+}, Co^{2+} and Cu^{2+} have toxicity or carcinogenicity issues and certainly cannot be used as food colorings. This means that colored organic compounds must be sought but most are also hazardous in some way. In fact the number of colored organic compounds that can be used as food colorings comprise a very short list.

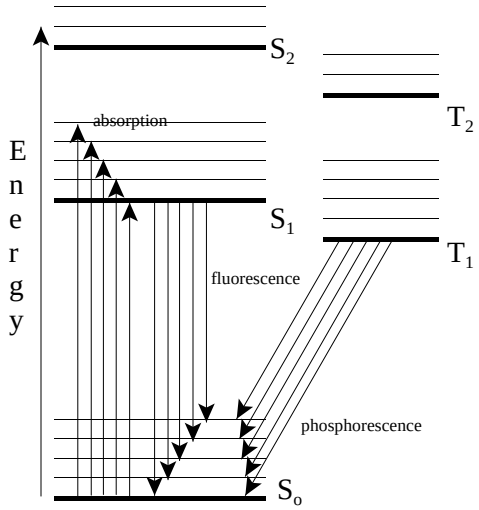
The dyeing of fabrics was recorded as early as 2600 BC in China and was undoubtedly practiced long before that time. Natural dyes such as indigo dominated the dyeing process until William Henry Perkin's discovery of the first synthetic dye, mauve, in 1856. This was another example of a serendipitous discovery as Perkin had actually been searching for a cure for malaria. Subsequent to mauve, many dyes have been developed. Today, after synthesizing a dye (rhodamine B), you will briefly experiment with dyeing techniques using your synthesized dye and a multifiber testfabric that contains 6 different types of material.



Rhodamine B

For a colored compound to be a useful dye, there must be ways of binding the dye strongly and evenly to the fabric. Repeated washing should not significantly diminish the color. There are different methods that can be used to provide "fastness" to the dyeing process. The effectiveness of each procedure depends on the nature of the fabric and the dye. There are at least four methods of dyeing that are commonly used: direct, mordant, developed and vat. Direct dyes adhere by themselves to the fabric. Mordant dyes need an intermediary chemical that bonds to the fabric and then the mordant dye bonds to the intermediary chemical. Developed dyes are chemicals that are bonded to the fabric and then converted via chemical reaction to colored compounds. Since vat dyes are insoluble in their colored or oxidized from, they are applied in a soluble, reduced form and then oxidized after bonding has occurred to a colored form. The success of dyeing with rhodamine B will be compared on several fabrics using a direct dyeing technique.

In addition to its property as a potential dye, rhodamine B is a strongly fluorescent compound. Fluorescence is initiated by the absorption of a photon. The resulting excited state generally has a lifetime of nanoseconds to microseconds. For some compounds, the excited state loses the energy that resulted from absorption by emitting a photon. This emission is called fluorescence. The energy of the fluorescence must be equal to or lower than the energy of the light that was absorbed. Often this results in a fluorescence that is a very rough mirror image of the lowest energy absorption band.



Jablonski diagram *Fig. 30-2*

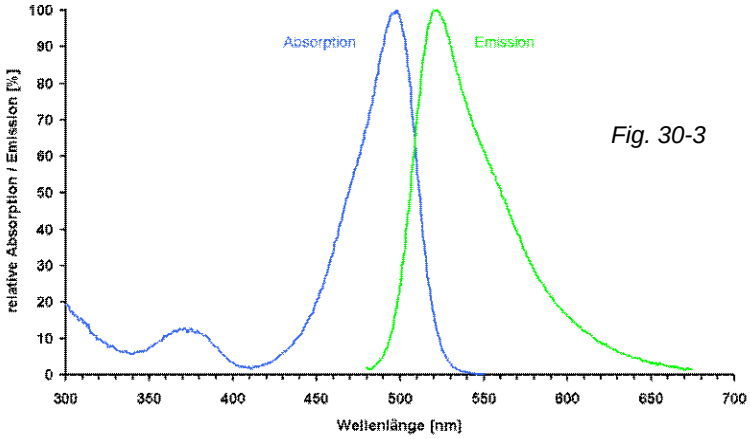


Fig. 30-3

Procedure

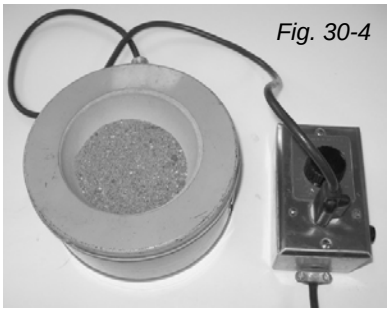
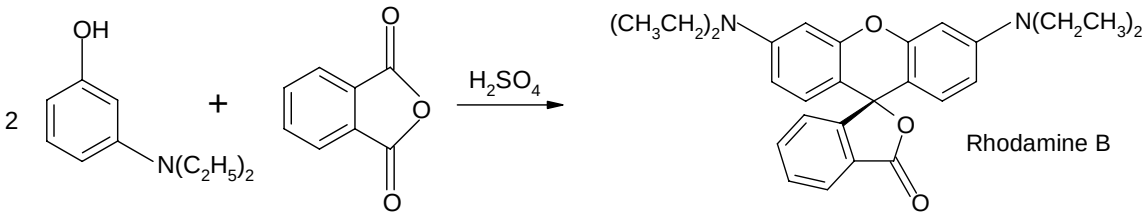


Fig. 30-4

[Alert: Please note the product, rhodamine B is a suspected carcinogen and contact with it should be avoided.] Transfer enough sand to a 500 mL heating mantle to fill the mantle to about the $\frac{2}{3}$ level. The heating mantle can be used by several students. Adjust the voltage or power control until the temperature stabilizes somewhere between 180° and 200°C. To prepare rhodamine B, add 230 mg of 3-(diethylamino)-phenol to a mortar. Add 100 mg of phthalic anhydride to the mortar and throughly grind and mix the two solids together. Transfer the mixed soldis to a large test tube (15 x 100 mm). Add three drops of 2 M H_2SO_4 (or 2 drops of 3 M H_2SO_4) and 1 drop of water to the mixture and stir again. Place the test tube in the preheated sand bath for about 60 minutes. This time period was suggested by the reference. It is possible that shorter times will suffice and this could be the subject of a class study. Try to maintain the temperature between 180° and 200°C.



After heating for about 1 hour, remove the test tube from the sand bath and allow it to cool for several minutes and then place the test tube in an ice bath to cool it to room temperature. Add 3 mL of methylene chloride to the tube and stir thoroughly. Decant the methylene chloride layer into a small separatory funnel. Add 3 mL more of methylene chloride to the residue in the test tube, stir, and decant into the separatory funnel. Repeat the methylene chloride extraction of the residue two more times giving approximately 12 mL of methylene chloride in the separatory funnel. Extract the organic layer with 10 mL of 10% sodium bicarbonate solution followed by two extractions with 10 mL of water. Be sure you save the organic layer each time and properly dispose of the aqueous layers. Dry the methylene chloride layer over sodium sulfate and evaporate to dryness using a rotary evaporator. If the product remains tacky, place it in your lab drawer with the top of the container open and allow it to dry until your next lab period. After it is dry, determine the mass, yield and uv-visible spectrum of the product. From the spectrum, determine if you have successfully synthesized rhodamine B.

UV-Visible Spectrum of the Dye and Fluorescence. Weigh out about 2 mg of the dye and transfer it to a 10 mL volumeteric flask. Dissolve the solid in methanol and add methanol to the mark. Use a 250 μL syringe or 0.5 mL pipet to transfer 0.1 mL of the dye solution to a 5 mL volumetric flask and dilute to the mark with methanol. Run the UV-visible spectrum from 700 nm to 300 nm or as low as your instrumentation will allow (depends on cell material and type of instrument). Compare your results to the spectral information below to determine if your synthesis was successful. Take the cell containing your dye solution into a room that can be darkened and expose it to a black light. Report your observations including a description of the color.

> The absorption and emission spectra of Rhodamine B are roughly mirror images of each other with the absorption maximum at 550 nm and the fluorescence maximum at 580 nm. There is also a shoulder in the absorption at about 510 nm and a corresponding shoulder in the emission at about 620 nm.

Dyeing.

Direct dyeing. A solution containing about 0.01 g of the dye in 20 mL of deionized water should be prepared. Boil the solution and using tongs, dip a multifiber Testfabric 10A into the boiling solution for about 2 minutes. Wash the testfabric with cold water and determine which if any of the fabrics hold their colors. It might also be interesting to take the fabric into a dark room and irradiate it with a uv light to determine if the fluorescence is observed from the absorbed rhodamine B and whether it depends on the cloth type.

Note: Testfabric 10A has the following materials in the order given:

Filament Acetate Bleached Cotton Polyamide Spun Polyester Polyacrylic Worsted Wool

References

McCullagh, J. V.; Daggett, K. A. *J. Chem. Ed.* **2007**, *84*, 1799-1802.
http://www.pnas.org/cgi/reprint/17/8/480.pdf
http://omlc.ogi.edu/spectra/PhotochemCAD/html/rhodamineB.html
http://www.testfabrics.com/index.html

Prelaboratory Preparation - *Experiment 30*

First, be sure to list all the goals of the experiment. Prepare a table for insertion of useful and observed data such as molecular mass, mass, moles, melting points and percent yields and recoveries. Look up the meaning and origin of fluorescence. Locate the electrophilic aromatic substitution reaction involved in the synthesis on the *Reaction-Map of Organic Chemistry* in ***Appendix C*** and include the reaction number in your report.

Observations

Report all relevant observations including masses, color and dyeing observations and the absorption spectrum. Be sure to carefully report the color of each type of cloth, the color of the rhodamine B solution and the color of the fluorescence.

Conclusions

This section should include the following:

1. Were the goals of the experiment achieved? Explain your answer.
2. What evidence do you have that your synthesis was successful?
3. How could the percent yield and recovery have been improved?
4. Report on the success of the dyeing for each type of fabric. Try to explain the differences.
5. The color of the rhodamine B solution is the result of the light that is not absorbed by the solution. Does this color agree with the absorption spectrum that you recorded?
6. Based on the absorption spectrum, what color would you expect for the fluorescence? Did your observations agree with expectations?
7. Include a detailed mechanism for each of the reactions involved in the synthesis. Explain why one of the reactions can be called a Friedel-Crafts reaction.